

$$\frac{\partial \psi}{\partial \tau} = \left(\frac{\kappa_{diff}}{\epsilon \alpha} \right) \left[\frac{1}{\frac{1}{\alpha} + \frac{\kappa_{ads}}{(1 + \kappa_{ads} \psi)^2}} \right] \left[\frac{\partial^2 \psi}{\partial \lambda^2} - \phi^2 \frac{\psi}{(1 + \kappa_{ads} \psi)^2} \right]$$

$$\psi = \frac{C_A}{C_{A,max}} = \text{gas-phase reactant concentration}$$

$$\tau = t(s)k_{-1}(s^{-1}) = \text{dimensionless time}$$

where k_{-1} is the reactant desorption rate constant in step 1.

$$\kappa_{diff} = \left(\frac{D_e}{L^2} \right) \left(\frac{1}{k_{-1}} \right) = \text{dimensionless diffusion coefficient in layer of thickness } L$$

$$\kappa_{ads} = \frac{k_1(\text{m}^3 \text{mol}^{-1} \text{s}^{-1})C_{A,max}(\text{mol m}^{-3})}{k_{-1}(\text{s}^{-1})} = \text{reactant adsorption rate constant}$$

$$\kappa_{rxn} = \frac{k_2(\text{s}^{-1})}{k_{-1}(\text{s}^{-1})} = \text{reaction rate constant}$$

ϵ = void fraction in porous catalyst layer

$$\alpha = \frac{A(\text{m}^2)C_{A,max}^{\text{surface}}(\text{mol m}^{-2})}{\epsilon V(\text{m}^3)C_{A,max}^{\text{gas}}(\text{mol m}^{-3})} = \text{surface-to-gas capacity ratio}$$

$$\lambda = \frac{z(\text{m})}{L(\text{m})} = \text{position within layer}$$

Square of Thiele Modulus:

$$\phi^2 = \left(\frac{\kappa_{rxn} \kappa_{ads}}{\kappa_{diff} / (\epsilon \alpha)} \right) = \frac{L^2}{D_e} [k_2(A/V) \kappa_{ads} C_{A,max}^{\text{surface}}] = \frac{L^2(\text{m}^2)}{D_e(\text{m}^2 \text{s}^{-1})} [K_r(\text{s}^{-1})]$$

$$\text{At steady state: } \frac{\partial^2 \psi}{\partial \lambda^2} = \phi^2 \frac{\psi}{(1 + \kappa_{ads} \psi)^2}$$

$$\theta_{AS} = \frac{\kappa_{ads} \psi}{1 + \kappa_{ads} \psi} = \text{local coverage of surface by adsorbed A ; local reaction rate} = \frac{\kappa_{rxn} \kappa_{ads} \psi}{(1 + \kappa_{ads} \psi)^2}$$

Match catalyst layer to mixing cell:

$$\left(\frac{V_{cell}}{V_{layer}} \right) \frac{d\psi_c}{d\tau} = \kappa_{flow}(\psi_{in} - \psi_c) - \kappa_{diff} \left[\frac{d\psi}{d\lambda} \right]_{\lambda=1} \quad \text{where } \psi_c = \text{reactant in mixing cell}$$

$$\kappa_{flow} = \frac{Q}{V_{layer} k_{-1}} = \frac{Q}{V_{cell} k_{-1}} \left(\frac{V_{cell}}{V_{layer}} \right) \quad \text{where } Q(\text{m}^3 \text{s}^{-1}) = \text{flow rate through mixing cell}$$

Local reaction rate as dimensionless turnover frequency (TOF):

$$\begin{aligned} \text{local d'less TOF} &= \frac{\text{mol A reacting}}{(\text{mol surface sites})(\text{dimensionless time})} \\ &= \frac{\kappa_{rxn} \kappa_{ads} \psi}{(1 + \kappa_{ads} \psi)^2} \end{aligned}$$

Average reaction rate in catalyst layer as dimensionless turnover frequency (TOF):

$$\begin{aligned} \text{average d'less TOF} &= \int_{\lambda=0}^{\lambda=1} \frac{\kappa_{rxn} \kappa_{ads} \psi}{(1 + \kappa_{ads} \psi)^2} d\lambda \\ &= \left(\frac{\kappa_{diff}}{\alpha \epsilon} \right) \int_{\lambda=0}^{\lambda=1} \frac{\phi^2 \psi}{(1 + \kappa_{ads} \psi)^2} d\lambda \quad \text{transient or steady state} \\ &= \left(\frac{\kappa_{diff}}{\alpha \epsilon} \right) \int_{\lambda=0}^{\lambda=1} \frac{d^2 \psi}{d\lambda^2} d\lambda \quad \text{at steady state} \\ &= \left(\frac{\kappa_{diff}}{\alpha \epsilon} \right) \left[\frac{d\psi}{d\lambda} \right]_{\lambda=1} \quad \text{using boundary condition } \left[\frac{d\psi}{d\lambda} \right]_{\lambda=0} = 0 \end{aligned}$$